



## **Voltammetric and coulometric techniques to estimate the electrochemical reaction rate during ohmic sterilization**

T. TZEDAKIS\*, R. BASSEGUY and M. COMTAT

*Laboratoire de Génie Chimique, UMR CNRS 5503, Université Paul Sabatier, 118, Route de Narbonne, 31062 Toulouse Cedex, France*

*(\*author for correspondence, e-mail: tzedakis@lgc.ups-tlse.fr; fax: +33 5 61556139)*

Received 23 July 1998; accepted in revised form 1 December 1998

**Key words:** electrochemistry, foods, heating, ohmic, sterilization

### **Abstract**

The ohmic process uses alternating current to heat rapidly and uniformly samples of food to be sterilized, but this process must not modify the organoleptic properties of the food. The aim of this work is to examine whether reactions occur between the electrodes and the various food compounds. The redox behaviour of several commercial foods in contact with various electrodes was examined and experiments were performed to elucidate the interfacial phenomena and to estimate the electrode reaction rate. The main result is that, at a frequency of 50 Hz, the Ti–Pt material has no significant electrocatalytic properties towards foods.

### **1. Introduction**

Common sterilization processes, such as UHT (ultra-high temperature) expose products to a temperature of about 130 °C for several minutes, although some fragile food compounds may be degraded faster than the microorganisms to be eliminated. Such is the case for some acids contained in milk, as was shown by Kessler et al. [1].

In the liquid phase, heat propagates by conduction and convection, whereas in the solid phase heat travels by conduction. Under these conditions, the compounds have to be exposed to high temperatures for long periods and this can significantly deteriorate the organoleptic properties such as taste and flavour, as well as the appearance of the food. The constantly growing demand for canned foods and precooked meals has led the food industry to develop new sterilization processes to treat solid–liquid mixtures and thus obtain products of better quality.

A new process for sterilization by ohmic heating has been developed under license by Baker [2] in the United Kingdom. Food flows in a cylindrical set-up equipped with electrodes to apply an alternating current (frequency 50 Hz). The current flow induces a Joule effect which rapidly ensures uniform heating of the

food in the region where the electrical field is applied and thus sterilizes the mixture without damaging the solid particles.

For a given current, the electrical power increases with the internal resistance of solid zones; consequently, the rate of heat production is higher in these zones and the temperature of the food increases rapidly without damaging the texture or flavour. In the case of alternating current the whole electrical power must be dissipated by the Joule effect. However, this can result in problems due, on the one hand, to the irreversible electrochemical degradation of the products at the electrode surface and, on the other hand, to deterioration of the electrodes by corrosion or abrasion.

An electrochemical study using direct and alternating currents was performed by Dupont et al. [3] for fatty acids. Results clearly showed that for frequencies of 50 Hz, the existence of reactions at the electrode depended on the nature of the electrode. In other studies, fatty acids appear to be easily oxidized electrochemically or chemically [4, 5]; the duplication of the radicals formed at the electrode or the autooxidation of the oils can cause peroxidation and form compounds responsible for making foods rancid and possibly at the root of diseases. Consequently, any electrochemical oxidation or reduction is undesirable in this type of

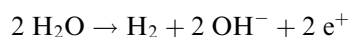
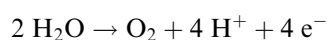
process and the electrochemical behaviour of foods under direct and alternating currents must be known so that, in industrial applications, products can be avoided that might react at the electrode during ohmic treatment. Food products are usually a mixture of several compounds and it is not possible to study each compound separately. Moreover the study of the redox behaviour of pure compounds is not representative of the food, as possible interactions between compounds are liable to modify this behaviour.

The aim of this electrochemical work is to study foods to be sterilized by ohmic heating and to seek the existence of reactions at the electrode with a view to validate the process on the pilot plant scale. More specifically, current–potential curves have been recorded with direct and alternating currents and two different electrodes in order to understand and identify the interface phenomena occurring during the ohmic heating process. Material balances for long term electrolyses are performed in order to quantify the reaction rate during the ohmic heating process.

## 2. Electrochemical phenomena at the electrodes during the application of an alternating electrical field

During ohmic heating, the electrodes are submitted to relatively high current densities ( $200 \text{ A m}^{-2}$ ) and temperatures ( $130\text{--}150^\circ\text{C}$ ). Under these conditions several phenomena can take place at their surface, in particular:

- (i) The electrochemical reaction of the solvent. Most food products contain water which can react electrochemically and this can result in the dangerous simultaneous production of hydrogen and oxygen due to the alternating polarity;



- (ii) The reduction of oxygen may lead to  $\text{O}_2^-$ . Formation of free radicals, such as  $\text{OH}^\cdot$ , due to Fenton's reaction [6], can then occur and cause oxidation of some substrates of the foods thus making them rancid.
- (iii) The direct oxidation or reduction of some electroactive foods can generate undesirable products that will modify the organoleptic properties of the foods [4];
- (iv) Oxidation of the electrodes can generate ions in solution or insulating species at the electrode, as in the case of rutile formed by oxidation of titanium electrodes [7].

Thus, the electrode can be partially passivated, overheating points can appear and some local degradation of the foods may be observed.

## 3. Influence of the frequency of the alternating current on electrochemical cell behaviour

Taking into account only one electrochemical reaction, the electrode may be represented by the circuit in Figure 1. This includes the resistance of the electrolyte solution ( $R_e$ ) in series with a dipole: resistance  $R_t$  and capacity  $C$  in parallel.  $C$  is the capacity of the electrochemical double layer and the resistance  $R_t$  is related to the charge transfer at the electrode.

First, some microseconds after the application of the potential to the electrode, polarization of the electrode–solution interface takes place and the greater part of the current is used to charge the capacitor. When the interface is polarized, electrochemical reactions take place and a faradaic current is generated. At any time total current is given by:

$$I_{\text{total}} = I_{\text{resistive}} = I_{\text{faradaic}} + I_{\text{capacitive}}.$$

When the polarity of the potential is reversed, the metal–solution interface behaves like a capacitor which charges and discharges. Ohm's law for alternating current is written  $U = (Z + R_e)I$  where  $Z$  is the impedance of the ( $R_t - C$ ) circuit and  $R_e$  the electrolytic resistance.

Ohm's law applied to circuit  $R_t - C$  is:  $U = Z(I_1 + I_2)$ . Replacing  $I_1$  and  $I_2$  by the expressions:  $I_1 = UjC\omega$  and  $I_2 = U/R_t$  [8] leads to the following relationship for the impedance:

$$Z = \frac{1}{jC\omega + \frac{1}{R_t}}.$$

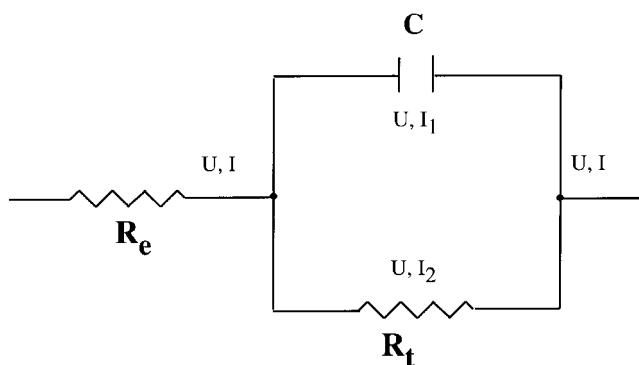


Fig. 1. Electrical circuit equivalent for an electrode;  $U$ : delivered voltage (V);  $C$ : Electrochemical double layer capacity (F);  $R_t$ : charge transfer resistance ( $\Omega$ );  $R_e$ : Electrolyte resistance ( $\Omega$ ).

At a high frequency  $N$  (or high pulsation rate  $\omega = 2\pi N$ ),  $jC\omega$  becomes very high and minimizes the  $Z$  value compared to the electrolyte resistance  $R_e$ . The electrochemical cell then behaves like a resistance. The limiting phenomenon of the overall process is the flow of current through the sample to be sterilized.

Impedance measurements allow the ratio of capacitive to faradaic current to be determined using the following expression in the Nyquist formalism

$$\frac{Z_{\text{imaginary}}}{Z_{\text{real}}} = -\frac{I_{\text{faradaic}}}{I_{\text{capacitive}}}.$$

Some studies [2] have shown that the  $I_{\text{faradaic}}/I_{\text{capacitive}}$  ratio varied between 20 and 40%. Here we would verify these results by carrying out long duration electrolyses.

#### 4. Materials and methods

The electrochemical study was carried out with already sterilized commercial foods. Several foods were studied: tomato sauces, vegetable soups, béchamel sauce, mayonnaise, sauces containing solid fragments etc. (Table 1). These products are sold in various containers: glass jars, cartons or cans.

A generator able to provide triangular or sinusoidal signals of various periods was used (Figure 2). The potentiostatic setup contained a working electrode made of platinum or platinized titanium; the auxiliary electrode was either of carbon or platinum. The reference electrode was a saturated calomel electrode (SCE), inserted in a tube filled with a KCl solution and ending in a capillary located close to the working electrode. The platinum electrodes, working and auxiliary, were cleaned by flame burning before each experiment.

Cyclic voltammetry with direct current was used to study the foods already sterilized to obtain a first view of the possible electrochemical reactions. The applied potential was a linear function of time and the scan rate was higher than  $50 \text{ mV s}^{-1}$  in order to minimize the diffusion of the species formed at the electrode and to examine their reactivity during the reversal cycle.

In the alternating current study an oscilloscope was used to observe the variation of the current  $I = b \sin(\omega t + \phi)$  when an alternating potential  $E = a \sin \omega t$  was applied;  $a$ ,  $b$  and  $\phi$  are, respectively, the amplitudes and the phase shift. Initial and final potentials correspond to the peak-to-peak potential of the signal. Eliminating time from the potential and current relationship makes it possible to access the current–potential curve:

Table 1. Potential values of various signals obtained in oxidation or in reduction with commercial products, a platinum electrode and direct current

Model solutions – Foods		pH	Potential of signals/V vs SCE	
			Oxidation	Reduction
KCl 0.02 mol dm <sup>-3</sup>		6.03	0.90	–0.40: dissolved O <sub>2</sub>
Compote Blédina (Diepal–NSA France Danone)	Apple–Prune	3.90	H <sub>2</sub> ads.: –0.30	0.00 and 0.15
	Apple–Quince	3.41	0.50 and 0.80	–0.10
Pure Soup <sup>*</sup> Liebig (Campbell)		5.67	0.50 and 0.95	0.05 and –0.40
JardinVegetables. Coalfish Blédina (Diepal–NSA France Danone)		5.70	H <sub>2</sub> ads.: –0.50 0.90	0.07 and –0.20
		5.14	H <sub>2</sub> ads.: –0.50 0.90	0.10
Pastashells – ham and tomato (Nestlé France)		5.14	H <sub>2</sub> ads.: –0.50 0.90	0.10
Ravioli (Panzani–France)	Rich	5.35	0.50 and 0.95	–0.20 and –0.50
	Pure Beef	5.65	0.95	0.05 and –0.40
Sauces (Panzani–France)	‘bolognaise’	4.78	0.25, 0.50	0.07 and –0.20
	‘provençale’	4.31	0.95 and 1.25	–0.40
Béchamel lighten, Liebig (Campbell)		6.38	0.90 and 0.50	0.05 and –0.50
Amora Dijon Mayonnaise* (Amora–France)		3.87	0.45, 0.70 and 0.90	–0.90

$r = 100 \text{ mV s}^{-1}$

\*:  $r = 5 \text{ mV s}^{-1}$

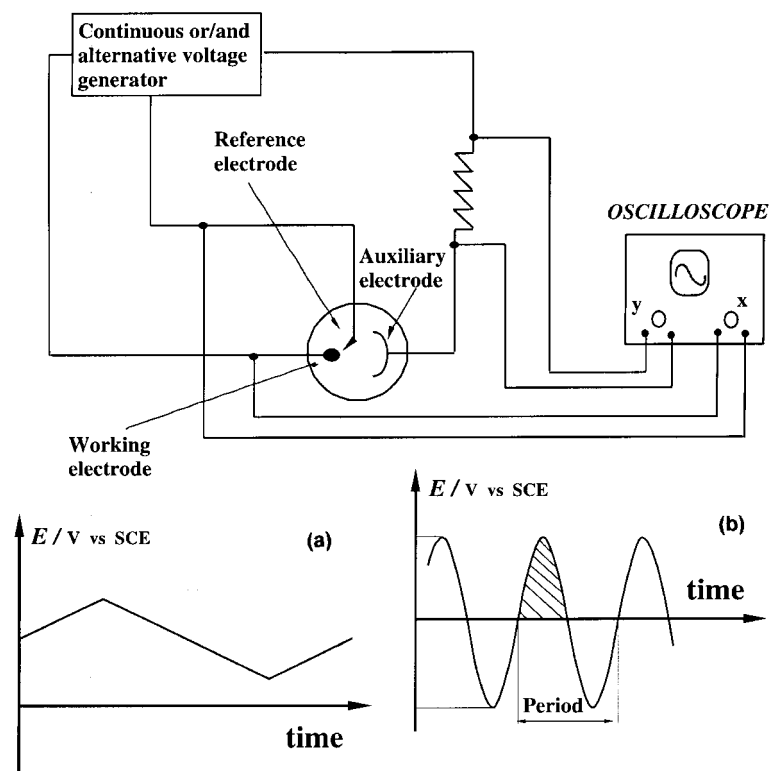


Fig. 2. Schematic representation of electrochemical setup used to plot current-potential curves. (a) Direct potential applied to the working electrode with respect to SCE as a function of time. (b) Alternating potential applied to the working electrode with respect to SCE as a function of time.

$$\frac{E^2}{a^2} + \frac{I^2}{b^2} - 2 \frac{EI}{ab} \cos \phi = \sin^2 \phi.$$

The Lissajous curves obtained are ellipses whose shape only depends on the phase shift  $\phi$ . If there is no phase shift between current and potential ( $\phi = 0$ ), the above relationship becomes Ohm's law,  $I = (a/b)E$ , and the overall process is limited by the resistive phenomenon and electrical power is only dissipated by the Joule effect.

For long duration electrolyses the redox system  $I_2/I^-$  was chosen because of its well known reversible electrochemical behaviour and because it can be used in the pilot plant without contaminating it.

The following electrolyses are performed:

- on the laboratory scale in a batch stirred reactor. electrical power = 5 W;  $V_{\text{treated}} = 1 \text{ dm}^3$ ;  $S_{\text{electrode}} = 210 \text{ cm}^2$ ; peak-to-peak potential =  $\pm 5 \text{ V}$ ; the current obtained varied from  $-1$  to  $+1 \text{ A}$ .
- on the pilot plant scale in a plug flow reactor ( $l = 1.8 \text{ m}$ ) equipped with three electrodes uniformly located. Electrical power = 10 kW;  $V_{\text{treated}} = 270 \text{ dm}^3$ ;  $S_{\text{electrode}} = 3 \times 210 \text{ cm}^2$ ; peak-to-peak potential =  $\pm 500 \text{ V}$ ; the current obtained varied from  $-20$  to  $20 \text{ A}$ .

The potassium iodide solution ( $\text{KI}$ :  $0.1 \text{ mol dm}^{-3}$ ) was submitted to electrolysis for one day and the concentration of the iodine ( $\text{I}_2$ ) formed was measured by U.V.-vis. spectroscopy at wavelengths 352 nm ( $\epsilon = 27300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 288 nm ( $\epsilon = 39810 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

## 5. Results

### 5.1. Voltammetric study on platinum

The electrochemical behaviour of several foods was studied, first with direct current to select those which present an anodic or cathodic electroactivity and then with an alternating current to show up any redox reactions due to sterilization.

Figure 3 shows the voltammogram obtained on platinum with tomato sauce 'Provençale sauce' with direct and alternating currents for various scan rates (5 and  $100 \text{ mV s}^{-1}$ ) and various frequencies (0.025 to 50 Hz) respectively. In the steady state the voltammogram shows four signals in oxidation at the following potentials: 0.25, 0.50, 0.95 and 1.25 V and one cathodic signal

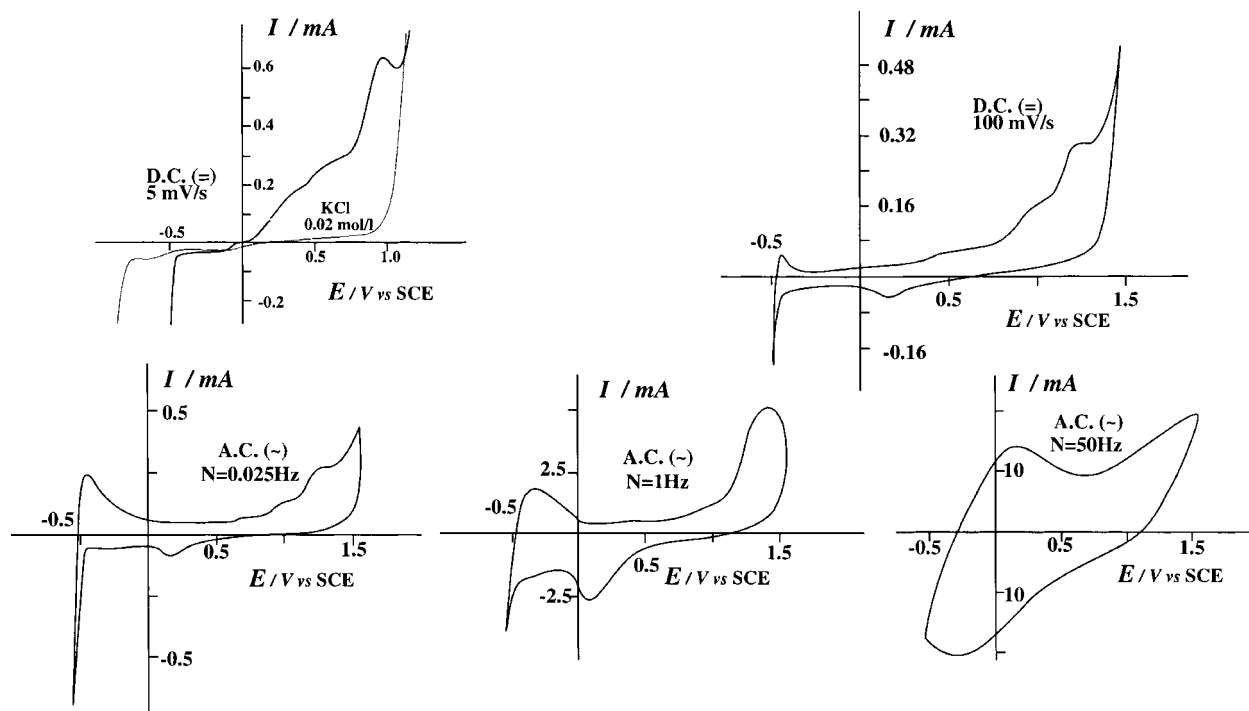


Fig. 3. Current-potential curves obtained on a platinum wire electrode ( $l_{\text{Pt}} = 1$  cm;  $\phi = 0.05$  cm) with Panzani 'provençale' sauce for various scan rates (direct potential) and various frequencies (alternating potential). Auxiliary electrode: Pt; reference electrode: SCE;  $\theta = 20^\circ\text{C}$ .

located at  $-0.1$  V. The species responsible for these current peaks were not identified.

The exponential variations of the current at  $-0.5$  V (direct and alternating current) and  $1.1$  V (direct current) or  $1.5$  V (alternating current) correspond to the reduction and oxidation of water. In fact when the potential of the electrode reaches these values, several bubbles appear in solution: production of  $\text{H}_2$  on the reduction side and  $\text{O}_2$  on the oxidation side.

The curves obtained with direct current (scan rate  $100\text{ mV s}^{-1}$ ) and with alternating current ( $N = 0.025\text{ Hz}$ ), plotted in the same potential range ( $-0.7$  to  $1.5$  V) during the same time (about  $20$  s), are similar and contain the same signals as the previous curve. Provençale sauce can therefore be oxidized on platinum with direct current or a low-frequency alternating current. Increasing the frequency reduced the number of observable current peaks. For  $N = 50\text{ Hz}$ , the curve is like an ellipse with two superposed peaks at  $0.2$  V for oxidation and  $-0.2$  V for reduction. The part of the curve located between  $-0.5$  and  $1.5$  V forms a tilted ellipse corresponding to a capacitive current due to the polarization of the interface.

At  $50\text{ Hz}$ , the electroactive system Provençale sauce/platinum is not entirely reversible as shown by the

nonsymmetrical anodic and cathodic peaks. This actually corresponds to an irreversible degradation of Provençale sauce during sterilization on platinum.

The electrochemical behaviour of several commercial products was studied on platinum under the same conditions as previously. The results with direct current are presented in Table 1 which gives the potential values of the peaks of the various signals found.

To sum up, all the curves obtained in cyclic voltammetry (as well as the curve obtained with a water-depleted sample such as mayonnaise) show: (i) an exponential part of curve for water oxidation and reduction, (ii) a peak corresponding to the reoxidation of adsorbed hydrogen ( $-0.5$  V) formed during the reduction of water, (iii) platinum oxidation at  $0.9$  V with formation of a platinum oxide, (iv) reduction of the dissolved oxygen gives a signal at  $-0.4$  V. This signal is, however, better defined in KCl solution than in food products. Finally, (v) the presence of three anodic signals and one cathodic one in the case of products containing tomato sauce proves that these foods are the most reactive and very easily oxidizable.

These results show the reactivity of various foods on a platinum electrode. Applying an alternating current with a frequency of  $50\text{ Hz}$  did not totally suppress

the reactions. Consequently, platinum cannot be used for ohmic sterilization processes using alternating current.

### 5.2. Voltammetric study on platinized titanium

The electrochemical behaviour of the products presented in Table 1 was examined at various frequencies ( $0.01 \text{ Hz} < N < 100 \text{ Hz}$ ) on platinized titanium. At low frequencies, although the current densities obtained on platinized titanium ( $\sim 2.5 \text{ mA cm}^{-2}$ ) were similar to those obtained on platinum ( $3.8 \text{ mA cm}^{-2}$ ), the results on Ti-Pt with Provençale sauce (Figure 4) were very different from those obtained on platinum (Figure 3). Indeed, the curve appears as a broad tilted ellipse with the two exponential parts of water oxidation and reduction and on which two main shoulder peaks are superimposed.

Increasing the frequency to 0.1 Hz removes these signals and the current-potential curve appears as an ellipse showing that the limitation of the overall current is due to capacitive and resistive phenomena with comparable rates.

For higher frequencies (10–100 Hz) the curves obtained are practically straight lines, showing the resistive

nature of the current. Similar results were obtained with  $\text{Na}_2\text{SO}_4$  solution and all foods presented in Table 1 (containing beef, tomato sauce, vegetables, fish etc.). In all cases, when the frequency reaches 50 Hz, the voltammogram is a straight line and consequently the current supplied is used to heat the food.

Two parameters are thus shown to have an influence on the redox behaviour of foods: the nature of the electrode and the frequency of the alternating signal applied. Although these results were obtained for an electrical power of about 1 W ( $S_{\text{electrode}} = 210 \text{ cm}^2$ ), they were confirmed for higher powers of the order of 10 kW ( $S_{\text{electrode}} = 3 \times 210 \text{ cm}^2$ ) similar to those used on an industrial scale. In the latter case, the potential of the working electrodes was varied from 0 to 500 V vs SCE.

Ohmic sterilization can be performed without any electrochemical reaction being measurable using this technique. Nevertheless, this approach remains qualitative and the reaction rate at the electrode cannot be determined. In fact this technique could not allow an estimation of the capacitive to faradaic current ratio, and a low faradaic current can be masked by a high resistive current.

### 5.3. Long duration electrolysis on the laboratory scale

Long duration (about one day) electrolyses of a  $0.1 \text{ mol dm}^{-3}$  potassium iodide solution with alternating current and 5 W electrical power ( $S_{\text{electrode}} = 210 \text{ cm}^2$ ;  $V_{\text{treated}} = 1 \text{ dm}^3$ ; peak to peak potential:  $\pm 5 \text{ V}$ ; current variation:  $\pm 1 \text{ A}$ ) were performed in order to quantify any variation in iodine concentration and to determine the electrochemical reaction rate. The results are shown in Figure 5 which gives the concentration of the iodine ( $\text{I}_2$ ) formed according to the reaction:  $2 \text{I}^- \leftrightarrow \text{I}_2 + 2 \text{e}^-$  and if there is an excess of iodide  $3 \text{I}^- \leftrightarrow \text{I}_3^- + 2 \text{e}^-$ .

The iodine concentration increased during electrolysis and reached  $2 \times 10^{-4} \text{ mol dm}^{-3}$  after 24 h (Figure 5(a)). The quantity of iodine formed during one current cycle (1/50 s) decreased from  $10^{-9}$  to  $10^{-10}$  moles in 24 h (Figure 5(b)). Consequently, for about two minutes (the time required for sterilization) the amount of iodine formed was lower than  $0.4 \mu\text{mol}$  (or 0.1 ppm) and appears negligible.

Integration of the curve  $I = b \sin(\omega t + \phi)$  gives the total charge transferred  $Q_{\text{theor}}$ . The experimental determination of the amount of iodine by ultraviolet spectroscopy made it possible, using Faraday's law, to determine the experimental charge actually used for the electrochemical reaction ( $Q_{\text{exp}}$ ). The ratio  $Q_{\text{exp}}/Q_{\text{theor}}$  decreased from 2% after 1 min of electrolysis to 0.2% after 24 h. This small amount, in fact, corresponds to

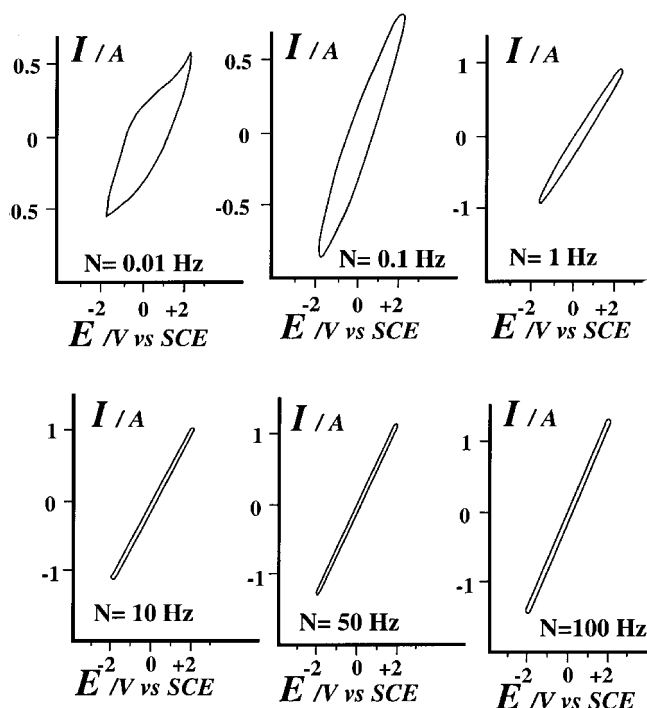


Fig. 4. Current-potential curves obtained on cylindrical platinized titanium electrode with Panzani 'provençale' sauce for various frequencies (alternating potential).  $S_{\text{Ti-Pt}}$ :  $210 \text{ cm}^2$ ; auxiliary electrode: carbon; reference electrode: SCE;  $\theta = 20^\circ \text{C}$ .

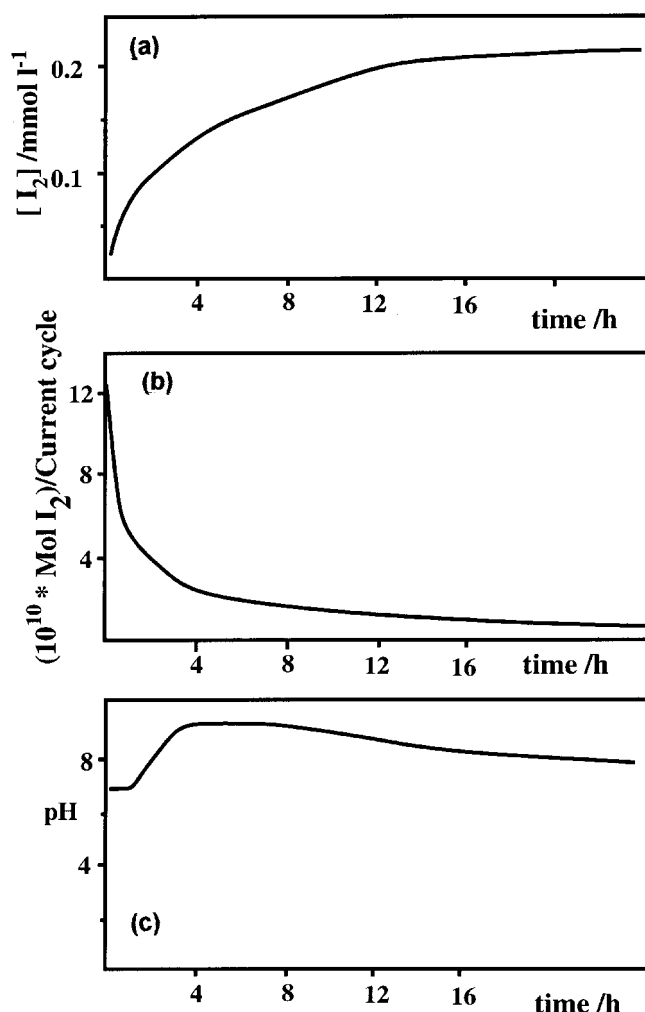


Fig. 5. Experimental results of a long duration electrolysis (with alternating current) of a potassium iodide  $0.1 \text{ mol dm}^{-3}$  solution ( $1 \text{ dm}^3$ ) on platinized titanium electrode.  $\text{N}_2$ : 1 atm; auxiliary electrode: C; Reference electrode: SCE; frequency 50 Hz;  $\theta$  increasing during electrolysis from  $25^\circ\text{C}$  to  $35^\circ\text{C}$ ; electrical power 5 W; electrode surface area  $210 \text{ cm}^2$  (a) Accumulated concentration of iodine formed as a function of time; (b) Molar quantity of iodine formed during one period of 0.02 s as a function of time; (c) pH evolution as a function of time.

the product formed that diffuses from the electrode to the solution before being converted again into the initial substrate.

The pH remained constant at the beginning of electrolysis ( $\sim 1 \text{ h}$ ) although the solution is not buffered. The two unit increase observed subsequently corresponds to a negligible rate for the protons consumed ( $\sim 1.3 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ ).

It can thus be concluded that if any electrochemical reactions do take place they can be considered as reversible when a high frequency alternating current is used.

#### 5.4. Long duration electrolysis on the pilot plant scale

The results obtained on the laboratory scale must be validated on the pilot plant scale. As described in Section 4, the principal differences between electrolyses on laboratory and pilot plant scales are as follows:

- (i) An electrical power approximately  $10^4$  times higher than that used for electrolysis on the laboratory scale  $\{P = 10 \text{ kW}\}$ .
- (ii) A total electrode surface area three times greater than that used for electrolysis on the laboratory scale ( $S_{\text{electrode}} = 3 \times 210 \text{ cm}^2$ ).
- (iii)  $270 \text{ dm}^3$  of potassium iodide instead of one litre ( $1 \text{ dm}^3$ ).

The results do not reveal the presence of iodine: the electrolytic solution remained colourless after addition of suspension of starch (detection threshold  $\sim 1 \mu\text{mol dm}^{-3}$ ). U.V-vis. spectroscopy also confirmed these results (detection threshold  $\sim 0.3 \mu\text{mol dm}^{-3}$ ).

The discrepancies between the laboratory and pilot plant results can be explained by the following:

- (iv) the operating conditions used: although the electrode reactions are reversible, some part of the iodine produced can diffuse from the electrode to the solution. This quantity depends on the hydrodynamics and on the frequency of the alternating voltage applied but not on the electrical power. Consequently, assuming that the electrochemical reaction rates are the same in the two experiments, the quantity of iodine which diffuses from the electrode is three times greater in the pilot plant because of the ratio of electrode areas, but the concentration of the iodine accumulated in the  $270 \text{ dm}^3$  reactor is divided by 90 compared with the concentration in the batch reactor on the laboratory scale. This fact explains why the solution remains colourless in the pilot plant.
- (v) the presence of impurities in the pilot plant or/and in the water used to prepare the KI solution. The electrochemically formed iodine may react with these impurities, so that its concentration decreases.

These results suggest that under these conditions ( $P = 10 \text{ kW}$ ;  $N = 50 \text{ Hz}$ ) and for all the foods examined, sterilization can be performed without electrochemical reactions taking place at any appreciable rate.

## 6. Conclusion

The electrochemical behaviour of several commercial food products was examined with alternating and direct currents using two different electrode materials (Pt and

Ti–Pt). The results show that the nature of the metal and the frequency of the alternating current are the two important parameters. Indeed, for both the electrodes used, increasing the frequency from 0.01 to 50 Hz minimized the rate of the electrode reactions. Moreover, at 50 Hz on platinized titanium, none of the products showed electroactivity at a rate measurable by the electrochemical kinetic technique used.

Material balances for long duration electrolyses allow us to propose a value for the ration of the electrochemical reaction  $I^- \rightarrow I_2$ . For very short times (2–3 min required for ohmic sterilization of foods) this rate is negligible ( $0.001 \mu\text{mol min}^{-1} \text{cm}^{-2}$ ) and it cannot cause explosions due to the formation of a  $H_2/O_2$  mixture, or any significant transformation of foods. However, since high-yield radical reactions can take place, it will have to be verified that the very small quantity of electrochemically generated radicals does not, during long storage periods, result in significant changes.

The results obtained must be confirmed with a totally irreversible system and with other electrode materials, of high double-layer capacity. Under these conditions, measurements of the electrochemical reaction rate will

allow the ohmic heating process to be validated; this will be the object of future work.

### Acknowledgements

The authors would like to thank Dr A. Bergel for helpful discussions.

### References

1. H.G. Kessler and R. Fink, *Chem. Ing. Tech.* **57**(7) (1985) 610.
2. A.P.V. Baker Ltd, *UK Patents G 2 067 390 B* and *G 2 068 200 B* (1984).
3. M. Dupont, Doctorat de l'Université de Poitiers, France (1997).
4. W.E. Neff and E. Selke, *J. Am. Oil Chem. Soc.* **70** (1993) 157.
5. S. Torii and H. Tanaka, In: H. Lund and M.M. Baizer (eds) *Organic Electrochemistry: An Introduction and a Guide*, 3rd edn, Marcel Dekker, New York, (1991) 535.
6. R. Tomat and A. Rigo, *J. Appl. Electrochem.* **9** (1979) 301.
7. M. Pourbaix, *Atlas d'équilibres électrochimiques* Gauthier-Villars, Paris (1963).
8. A.J. Bard "Electroanalytical chemistry" Marcel Dekker, New York (1970) 5.